Letter to the Editor

Commentary on the article: "A new kinetic model for heterogeneous photocatalysis with titanium dioxide: Case of non-specific adsorption considering back reaction, by S. Valencia, F. Cataño, L. Rios, G. Restrepo and J. Marín, published in Applied Catalysis B: Environmental, 104 (2011) 300–304"

As claimed in the abstract, S. Valencia et al. say to have developed a "new kinetic model" for heterogeneous photocatalytic reactions, as an alternative to the well known Langmuir–Hinshelwood (L–H) model and to the Direct–Indirect (D–I) model, developed by us during the last 6 years as a comprehensive approach to the photocatalytic oxidation of dissolved substrate species, both chemisorbed and physisorbed onto semiconductor nanoparticles [1–4]. In fact, the "new kinetic model" is a sub case of the D–I model, developed on the basis of a mechanistic scheme represented by Eqs. (2)–(9) of Section 2, a precise reproduction of the sequence of interfacial reactions sustaining the D–I model (see Section 3 of Ref. [3]). The only difference between the D–I model and the "new kinetic model" concerns the reaction step involved in the so-called "back reaction" of electroreduction of $(RH^\bullet)_{aq}$ primary photogenerated species with photogenerated conduction band electrons (Eq. (9)). As next explained, although the D–I model does not refuse the existence of the "back reaction" invoked by Valencia et al. (see for instance Eq. (13) of Ref. [3]), it denies the actual influence of this step on the phototocatalytic oxidation process of non-chemisorbed substrate species.

1. Misconceptions of the "new kinetic model": the back reaction vs. the current doubling reaction

According to Valencia et al., and in agreement with the D–I model [1,2], the "current doubling" (c-d) reaction and the "back reaction", represented by Eqs. (8) and (9), respectively, are incompatible with each other, in the sense that an efficient "current-doubling" reaction implicates a inefficient "back reaction" and vice verse. However, the authors assume that for phenol (PhO) photooxidation $v_{back} \gg v_{c-d}$, something extremely improbable. In fact, taking into account that $v_{back} = k_{back}[(RH^\bullet)_{aq}][Ti^{3+}]$ and $v_{c-d} = k_{c-d}[(RH^\bullet)_{aq}][Ti^{4+}]$, and considering that $[Ti^{4+}] \gg [Ti^{3+}]$, while $k_{c-d} \approx k_{back}$, as the overlapping of filled PhO$^\bullet$ energy levels with empty levels of Ti^{4+} ions is comparable to that of empty PhO$^\bullet$ energy levels with filled energy levels of Ti^{3+} ions, actually it should be $v_{c-d} \gg v_{back}$ but not $v_{back} \gg v_{c-d}$. This means that the "current doubling reaction" instead of the "back reaction" should be considered when analyzing the photooxidation of non-chemisorbed species. There is experimental evidence that "current doubling" can be an efficient reaction in the photoelectrochemical oxidation of substrate species like formic acid and methanol [5]. However, attention must be paid to the fact that in photoelectrochemical experiments no initial but steady-state photocurrents are measured. When initial photooxidation rates are considered, as it is the case in photocatalytic experiments, and $[(RH_2)_{aq}] \gg [(RH^\bullet)_{aq}]$, the influence of both the "current doubling" and the "back reaction" on the value of $-d[(RH_2)_{aq}]/dt$ is negligible. Finally, considering that $E_{redox}(PhO/PhO^\bullet) \approx 1.25$ V vs. NHE at pH = 3 [6], and considering a reasonable reorganization energy $\lambda = 0.6$ eV, the overlapping of PhO$^\bullet$ energy levels with Ti^{3+} and Ti^{4+} electron donor and acceptor conduction band edge energy levels, at about -0.3 V vs. NHE, is extremely poor, v_{back} and v_{c-d} reaction rates should be negligible in comparison to indirect photooxidation rate (voxIT).

2. Analysis of Eqs. (15) and (16)

According to the authors, Eqs. (10)–(14) lead to Eqs. (15) and (16), something not at all evident. Even assuming that Eqs. (15) and (16) were properly obtained, a detailed analysis of Eq. (16) is worthy. Eq. (16) can be transformed into: $\phi = -A\left(\frac{d[(RH_2)_{aq}]}{dt}\right)^2 - B\left(\frac{d[(RH_2)_{aq}]}{dt}\right)$ (15$_1$), where $A = (\beta/k_0)(1 + (\gamma[(RH_2)_{aq}])^{1/2}/[(RH_2)_{aq}])$ and $B = (1/k_0)(2 + (1/2\gamma[(RH_2)_{aq}])/1 + (\gamma[(RH_2)_{aq}])^{1/2})$, both depending through $\beta = (k'_{r_1})/(k_{ox_1}k_{red}[O_{2(aq)}])$ and $\gamma = (k_{ox_1}k_{back})/(k_{ox_2}k_{red}[O_{2(aq)}])$ on the five parameters k'_{r_1}, k_{ox_1}, k'_{red}, k_{ox_2} and k_{back}, with real physical meaning and accurate values involved in the photocatalytic process. Importantly, these parameters cannot be considered as simple fitting constants susceptible of arbitrary values, as the authors apparently do.

In Fig. 5, Valencia et al. present a reasonable good fitting of Eq. (15) to the phenol photooxidation rate dependence on the initial phenol concentration and photon flux experimentally obtained by Emeline et al. [7]. However, no information on γ and β values is given by the authors. We asked then for such an essential information, but no response was obtained. In our opinion, such an attitude contravenes the most elemental rule involved in any scientific communication, as it is offering the information required for checking involved results.

Even accepting the "excellent fitting" shown in Fig. 5 between Emeline et al. experimental results and those predicted by Valencia et al. Eq. (16), this cannot be considered as a proof of the "new kinetic model" capability for correctly explaining phenol photooxidation kinetics. In fact, let us transform Eq. (16) into: $-\frac{d[(RH_2)_{aq}]}{dt} = \frac{(B^2+4A\phi)^{1/2}-B}{2A}$ (15$_1$). For low enough ϕ values within the experimental photon flow range, such that $4A\phi \ll B^2$, it must be $-d[(RH_2)_{aq}]/dt \approx 0$, while for high enough ϕ values, such that $4A\phi \gg B^2$, Eq. (15$_1$) becomes: $-\frac{d[(RH_2)_{aq}]}{dt} = \left(\frac{\phi}{A}\right)^{1/2} =$

$\left(\left(\frac{k_0}{\gamma\beta}\right)^{1/2}[(RH_2)_{aq}\phi]\right)^{1/2}$ (15_2). Let us compare Eq. (15_2) with the photooxidation rate expression

$$-\frac{d[(RH_2)_{aq}]}{dt} = (2a^{IT}k_0([(RH_2)_{aq}]\phi))^{1/2} \qquad (14_1)$$

which is obtained from Eq. (14) of Ref [3], the general photooxidation rate expression predicted by the D–I model in the absence of specific adsorption, under high enough photon flux (ϕ)

$$-\frac{d[(RH_2)_{aq}]}{dt} = ((a^{IT}[(RH_2)_{aq}])^2 + 2a^{IT}k_0\phi[(RH_2)_{aq}])^{1/2} - a^{IT}[(RH_2)_{aq}] \qquad (14)$$

Interestingly, it is realized that Eq. (15_2) and Eq. (14_1), representing the photooxidation kinetics according to the "new kinetic model" and the D–I model, respectively, display a similar square root dependence of the photooxidation rate on ϕ and substrate concentration ($[(RH_2)_{aq}]$), something expected taking into account that the "new kinetic model" represents a particular case of the D–I model.

The following question arises at this point: if Eq. (15_2) is able to fit phenol photooxidation data by Emeline et al. under a constant value of $(1/k_0\gamma\beta)^{1/2}$, why Eq. (14_1) is not, except when the a^{IT} parameter depends on ϕ and $[(RH_2)_{aq}]$? (see Fig. 13 of Ref [3]). Valencia et al. should be able to explain this incongruence.

As for the observed experimental dependence of a^{IT} on ϕ and $[(RH_2)_{aq}]$ [3], we have recently reached evidence that it can be explained on the assumption that phenol species are able to electronically interact with the TiO_2 surface in competition with water molecules, in such a way that in phenol photooxidation both direct transfer (DT) and indirect transfer (IT) mechanisms for interfacial electron transfer coexist under non-equilibrated chemical, adsorption–desorption conditions [8].

3. Is the "new kinetic model" able to correctly predict the photon flux dependence of the photooxidation rate under variable substrate concentration?

As shown in Fig. 5 of Valencia et al., a reasonable good fitting of their Eq. (16) to the experimental dependence of the initial photooxidation rate on the substrate concentration is obtained. However, this is not enough proof to validate the "new kinetic model". As shown in Fig. 1, even the L–H model provides a good fitting, although, as recognized by the authors, the L–H cannot be considered a suitable model from a mechanistic point of view, as it does not take into account the physical and chemical steps involved into the photocatalytic process as a whole. In fact, a main drawback of the L–H model concerns its limitation to develop a kinetic expression explicitly involving the photon flux. A main challenge for a new photocatalytic kinetic model is to be able to predict the photon flux dependence of the photooxidation rate. Curiously, although Eq. (16) of Valencia et al. "new kinetic model" explicitly incorporates the photon flux as a variable, no fitting of the V_{OX} vs. ϕ experimental dependence is presented by the authors.

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